

Calix[4]arene Based Single-Molecule Magnets**

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Single-molecule magnets (SMMs)^[1] have been the subject of much interest in recent years because their molecular nature and inherent physical properties allow the crossover between classical and quantum physics to be observed.^[2] The macroscopic observation of quantum phenomena - tunneling between different spin states,^[3] quantum interference between tunnel paths^[4] - not only allows scientists to study quantum mechanical laws in great detail, but also provides model systems with which to investigate the possible implementation of spin-based solid state qubits^[5] and molecular spintronics.^[6] The isolation of small, simple SMMs is therefore an exciting prospect. To date almost all SMMs have been made via the self-assembly of 3d metal ions in the presence of bridging/chelating organic ligands.^[7] However, very recently an exciting new class of SMMs, based on 3d metal clusters (or single lanthanide ions) housed within polyoxometalates,^[8] has appeared. These types of molecule, in which the SMM is completely encapsulated within (or shrouded by) a “protective” organic or inorganic sheath have much potential for design and manipulation: for example, for the removal of unwanted dipolar interactions, the introduction of redox activity, or to simply aid functionalisation for surface grafting.^[9]

Calix[4]arenes are cyclic (typically bowl-shaped) polyphenols that have been used extensively in the formation of versatile self-assembled supramolecular structures.^[10] Although many have been reported, *p*-But-calix[4]arene and calix[4]arene (TBC4 and C4 respectively, Figure 1A) are frequently encountered due to a) synthetic accessibility, and b) vast potential for alteration at either the upper or lower rim of the macrocyclic framework.^[11] Within the field of supramolecular chemistry, TBC4 is well known for interesting polymorphic behavior and phase transformations within anti-parallel bi-layer arrays, while C4 often forms self-included trimers.^[12] The polyphenolic nature of calix[*n*]arenes (where *n* = 4 – 8) also suggests they should be excellent candidates as ligands for the isolation of molecular magnets, but to date their use in the isolation of paramagnetic cluster compounds is rather limited.^[13] Herein we present the first Mn cluster and the first SMM to be isolated using any methylene bridged calix[*n*]arene - a ferromagnetically coupled mixed-valence [Mn^{III}₂Mn^{II}₂] complex housed between either two TBC4s or two C4s.

Reaction of MnBr₂ with TBC4 and NEt₃ in a solvent mixture of MeOH/DMF results in the formation of the complex [Mn^{III}₂Mn^{II}₂(OH)₂(TBC4)₂(DMF)₆] (**1**) which crystallises as purple blocks that are in the monoclinic space group *P*2₁/*c*. The cluster (Figure 1B) comprises a planar diamond or butterfly-like [Mn^{III}₂Mn^{II}₂(OH)₂] core in which the wing tip Mn ions (Mn1) are in the 3+ oxidation state and the body Mn ions (Mn2) in the 2+ oxidation state. This is a common structural type in Mn SMM chemistry,^[14] but the oxidation state distribution here is highly unusual, being “reversed” from the norm in which the body Mn ions are almost always 3+. Indeed the “reversed” core has been seen only once before, in the cluster [Mn^{III}₂Mn^{II}₂(teaH)₂(acac)₄(MeOH)₂]²⁺ (**2**) (teaH₃ = triethanolamine) and its analogues.^[15] The Mn³⁺ ions are in distorted octahedral geometries with the Jahn-Teller axes defined by O5(DMF)-Mn1-O6(OH). The four equatorial sites are occupied by the oxygen atoms (O1-O4) of the TBC4, two of which bridge in a μ₂-fashion to the central Mn²⁺ ions (Mn1-O4-Mn2, 103.5°; Mn1-O1-Mn2, 105.4°). These are connected to each other (Mn2-O6-Mn2', 94.7°) and to the Mn³⁺ ions (Mn1-O6-Mn2, 100.4°; Mn1-O6-Mn2', 98.8°) via two μ₃-bridging OH⁻ ions, with the two remaining equatorial sites (completing the distorted octahedral geometry on Mn2) filled by terminal DMF molecules. There are no inter-molecular H-bonds between symmetry equivalents of **1**, with the closest

interactions being between neighbouring DMF molecules at ca. 3.3 Å. The only intermolecular interaction with the core of **1** is from a disordered MeOH that hydrogen bonds to O4.

INSERT FIGURE 1 – 1 column

Notably, the orientation of the endo-TBC4 DMF molecule in **1** is atypical and is driven by coordination. To our surprise we could not find a report on the solid state structure of the DMF solvate of TBC4. Solvothermal re-crystallisation of TBC4 from DMF resulted in the formation of large colorless crystals that are in a tetragonal cell common for solvates of TBC4.^[16] Structural analysis shows the expected bi-layer arrangement in which the DMF molecules are oriented with methyl groups inserted into the calixarene cavity (Figures 2A and S1). For comparison, the extended structure of **1** (Figure 2B) shows a bi-layer type arrangement that is skewed relative to that in TBC4-DMF. This is likely attributable to the restriction on TBC4 orientation - that is dictated by cluster formation - in addition to the presence of the peripheral DMF ligands on Mn²⁺ and Mn²⁺ (Figure 1B). Furthermore, the almost completely encapsulated cavity bound DMF molecule in **1** should have little effect over bi-layer orientation relative to TBC4-DMF given that guest protrusion from the cavity is similar in both cases (Figures S2 and S3 respectively). Although the extended structure in **1** does deviate from true planarity, the clusters are nevertheless arranged in bi-layers that have an inter-layer separation of ~ 19 Å (Figure 2B).

INSERT FIGURE 2 HERE – 1 column

With respect to the magnetic properties of **1**, dc susceptibility measurements were carried out in the 300 - 5 K temperature range in an applied field of 0.1 T. The room temperature $\chi_M T$ value of 15.5 cm³ K mol⁻¹ is larger than the spin-only value expected for an uncoupled [Mn^{III}₂Mn^{II}₂] unit of 14.75 cm³ K mol⁻¹ (Figure 3). The value then increases very slowly with decreasing temperature reaching a maximum of ~25 cm³ K mol⁻¹ at 5 K. The behaviour - similar to that reported for other [Mn^{III}₂Mn^{II}₂] clusters - is suggestive of dominant but weak intra-molecular ferromagnetic exchange.^[14] The experimental data can be satisfactorily fitted using the (standard)^[14b] isotropic $2J$ model of Figure 3, affording the parameters $J_{bb} = -2.43$ cm⁻¹ and $J_{wb} = +1.84$ cm⁻¹ for $g = 2.0$ (fixed). With these parameters the spin ground state of the system is an $S = 7$ spin state (Figure S4), with numerous excited states lying just above it, defining a quasi-continuum of states. Interestingly the magnitude of the exchange interactions closely resembles that observed for **2**, but in that case distortions of the Mn²⁺-O-Mn²⁺ central core resulted in all the exchange interactions being very weakly antiferromagnetic.^[15] We also note that the exchange interactions are likely much smaller than the single ion zfs (weak exchange limit) and thus the low lying multiplets cannot properly be described as total S states.

INSERT FIGURE 3 HERE – 1 column

This picture is also reflected in the magnetisation versus field data (collected in the ranges 0.5 – 7.0 T and 2 – 7 K and plotted in the inset of Figure 3) which shows M increasing only slowly with H , rather than quickly reaching saturation as one would expect for an isolated spin ground state. This is indicative of the population of low lying levels with smaller magnetic moment, which only become depopulated with the application of a large field - and so we cannot describe the system within the giant spin approximation. Ac susceptibility studies carried out on crystalline samples of **1** in the 1.8-10.0 K range in a 3.5 G field oscillating at frequencies up to 1000 Hz (Figure S5) display the tails of frequency-dependent out-of-phase (χ_M'') signals (suggestive of SMM behaviour) but no peaks. Hysteresis loop measurements carried out on single crystals using a micro-SQUID assembly with the field applied along the easy axis of magnetisation,^[17] show temperature and sweep rate dependent hysteresis loops confirming SMM behaviour (Figure 4). The loops are indicative of a well-isolated SMM (*i.e.* no inter-cluster interactions) with quantum steps, but one in which many excited states are clearly mixed with the ground state, in agreement with the powder data above. In addition to the contribution of excited states, crystal defects, nuclear spins, dipolar interactions and/or disorder (if present) will also lead to the broadening of steps.

INSERT FIGURE 4 HERE – 1 column

To demonstrate generality, replacing TBC4 with C4 resulted in the formation of thin weakly diffracting purple crystals. X-ray diffraction studies showed the crystals to be of poor quality but afforded a partial structure. Formation of the C4 based SMM **3** core (analogous to **1**) was confirmed in the partial structure by observation of the main atomic positions (Figure 5). The extended structure shows that **3**, relative to **1**, assembles as a bi-layer with a markedly shorter inter-layer spacing of ~ 13.5 Å (Figure 5B). This reduced inter-layer spacing is likely due to both removal of the ^tBut groups from the upper rim and subsequent protrusion of the DMF methyl groups from the C4 cavity. As a result of cavity occupation, there appears to be no notable interactions between neighbouring C4s (Figure S6). This clearly shows that substitution at the calixarene upper rim has a dramatic effect on assembly within resulting bi-layers, and suggests that alteration of these groups may afford a degree of supramolecular control with this system.

INSERT FIGURE 5 HERE – 1 column

To conclude, we have presented the first Mn cluster/first SMM to be isolated using any methylene bridged calix[*n*]arene. This SMM formation is general for calix[4]arenes and given the vast range of methylene bridged derivatives available, this motif presents a virtually unbounded range of SMMs that possess huge scope for materials design. The calix[4]arenes provide a protective skin both above and below the SMM layer, and alteration to the upper rim properties of the calixarene framework will provide control over bi-layer packing, inter-layer spacing, and three dimensional order in general. Alteration of the guest in the calixarene cavity, and also the ligands at the peripheral Mn

coordination sites will provide further opportunities for controlling self-assembly and tuning of the magnetic properties of these new SMMs. This will be the focus of future studies, as will be obtaining a more accurate structure of **2** and examining its magnetic properties.

Experimental Section

MnCl₂·4H₂O (0.1 g, 0.5 mmol) and TBC4 (0.1 g, 0.15 mmol) were dissolved in a mixture of DMF (10 ml) and MeOH (10 ml) and stirred for 1 hour. X-ray quality crystals were obtained in good yield (40%) after slow evaporation of the mother liquor. Elemental analysis (%) calculated for C₁₀₆H₁₄₆Mn₄N₆O₁₆: C 64.30, H 7.43, N 4.24; Found: C 64.02, H 7.54, N 4.21.

Crystal data for TBC4-DMF: C₄₇H₆₃N₄O₅, *M* = 722.0, Colourless Block, 0.50 × 0.42 × 0.38 mm³, tetragonal, space group *P4/n* (No. 85), *a* = *b* = 12.6880(18), *c* = 13.001(2) Å, *V* = 2093.0(5) Å³, *Z* = 2, Bruker Nonius X8 Apex II diffractometer, Mo-Kα radiation, λ = 0.71073 Å, *T* = 100(2)K, 2θ_{max} = 49.8°, 7253 reflections collected, 1825 unique (*R*_{int} = 0.0613). Final *GooF* = 1.134, *R*₁ = 0.0652, *wR*₂ = 0.1650, *R* indices based on 1340 reflections with *I* > 2σ(*I*) (refinement on *F*²). A number of restraints were applied due to disorder in the DMF guest molecule and the 'But groups of the TBC4. CCDC number: 741028.

Crystal data for 1: C₁₀₈H₁₅₄Mn₄N₆O₁₈, *M* = 2044.13, Purple Block, 0.44 × 0.38 × 0.20 mm³, monoclinic, space group *P2₁/c* (No. 14), *a* = 20.455(3), *b* = 11.2777(17), *c* = 24.513(4) Å, β = 111.871(2)°, *V* = 5247.8(13) Å³, *Z* = 2, Bruker Apex II CCD diffractometer, Synchrotron radiation, λ = 0.77490 Å, *T* = 100(2)K, 2θ_{max} = 50.4°, 42709 reflections collected, 7304 unique (*R*_{int} = 0.0868). Final *GooF* = 1.018, *R*₁ = 0.0551, *wR*₂ = 0.1418, *R* indices based on 5120 reflections with *I* > 2σ(*I*) (refinement on *F*²). CCDC number: 741029.

Unit cell parameters for partial structure of 3: Monoclinic, space group *P2₁/c* (No. 14), *a* = 12.6152(23), *b* = 12.5692(22), *c* = 28.1584(54) Å, β = 105.859(3)°, Bruker Apex II CCD diffractometer, Synchrotron radiation, λ = 0.77490 Å, *T* = 100(2)K. Crystal quality precluded full structural characterisation.

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Figure 1. a) Structure of the calix[4]arenes used in SMM formation. b) Single crystal X-ray structure of **1**. Selected atoms are labeled and H-atoms have been omitted for clarity.

Figure 2. a) Extended structure of TBC4-DMF. b) The extended structure of **1** showing the inter-planar separation between layers of clusters. Figures not to scale and hydrogen atoms omitted for clarity.

Figure 3. Plot of $\chi_M T$ versus *T* for **1**. The solid line is a fit of the experimental data using the cartoon scheme shown in the lower inset. Inset (top): Magnetisation (*M*/Nμ_B) vs *H* data in the 2-7 K and 0.5 – 7 T temperature and field ranges.

Figure 4. Hysteresis loops measured on single crystals of **1**, M is normalised to its saturation value.

Figure 5. a) Partial single crystal X-ray structure of **3**. b) The extended partial structure of **3** showing the inter-planar separation between layers of SMMs. Figures not to scale and hydrogen atoms omitted for clarity.

Keywords: Magnetic properties • Manganese • Supramolecular chemistry • Calixarenes • Self-assembly

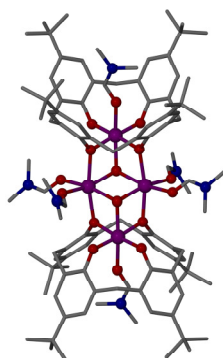
Layout 1:

((Catch Phrase))

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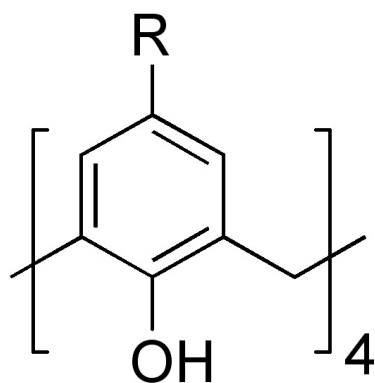
Calixarene Based Single Molecule
Magnets



New single molecule magnets that are protected by two calix[4]arenes have been synthesized. Alteration of the calixarene upper rim demonstrates supramolecular isolation and control over orientation in the solid state by altering the distances between layers of this new SMM motif.

Figure 1:

a)



R = ^tBut, TBC4
R = H, C4

b)

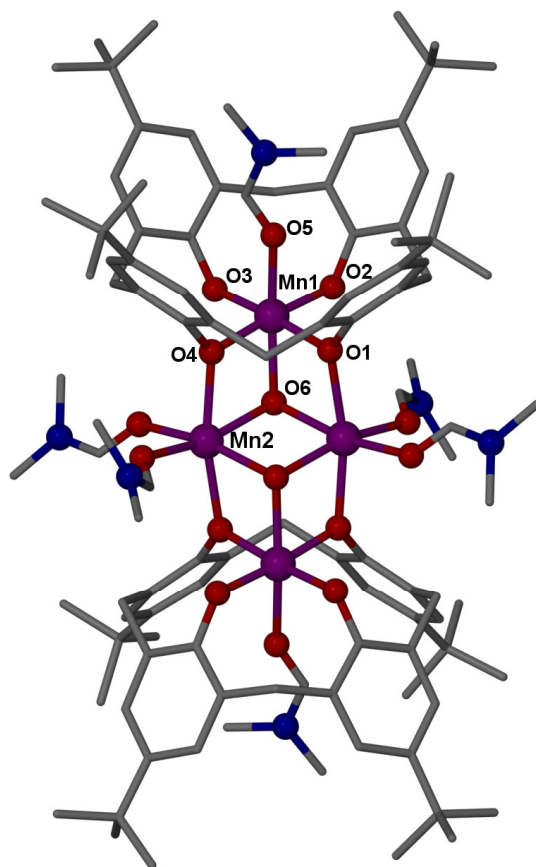
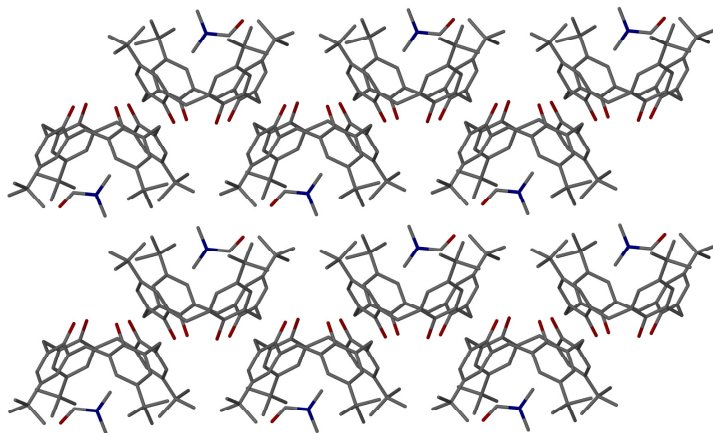


Figure 2:

a)



b)

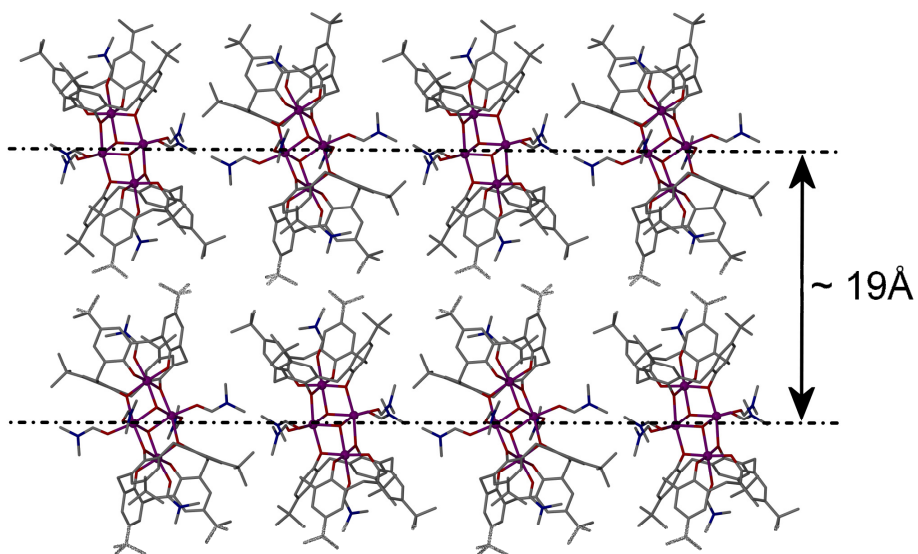


Figure 3:

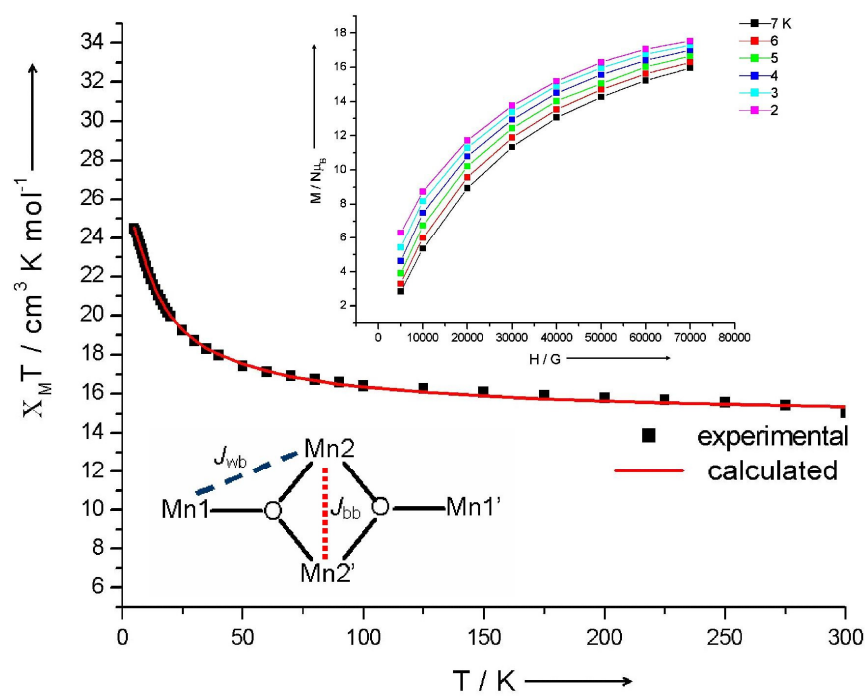


Figure 4:

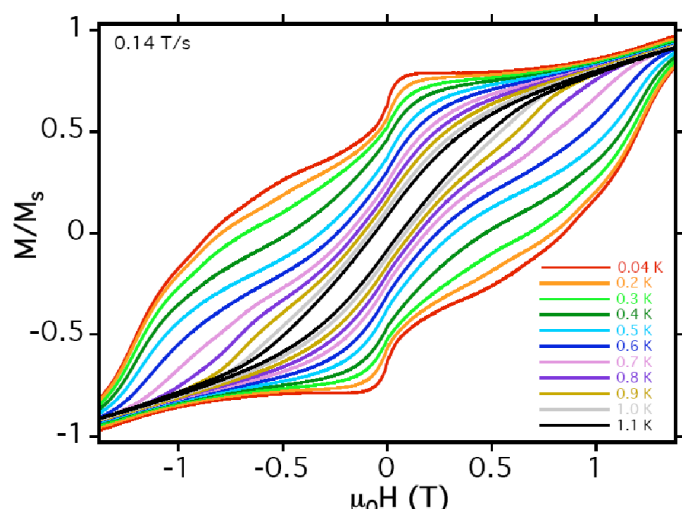


Figure 5:

